

Solubility of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ in the System $\text{Ca}(\text{OH})_2 - \text{H}_3\text{PO}_4 - \text{H}_2\text{O}$ at 5, 15, 25, and 37.5 °C*

Thomas M. Gregory,** Edgard C. Moreno,***, and Walter E. Brown****

Institute for Materials Research,
National Bureau of Standards,
Washington, D.C. 20234

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Solubility isotherms for $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$, dicalcium phosphate dihydrate, DCPD, in the ternary system $\text{Ca}(\text{OH})_2 - \text{H}_3\text{PO}_4 - \text{H}_2\text{O}$ were determined at 5, 15, 25, and 37.5 °C in the pH range 3.5–7; the relative positions of the isotherms indicate that DCPD has a negative thermal coefficient of solubility. The solubility product, K_s , of DCPD and the stability constants K_x and K_y for the ion pairs $[\text{CaHPO}_4^0]$ and $[\text{CaH}_2\text{PO}_4^+]$, respectively, were obtained as functions of temperature by the use of a generalized least squares procedure subject to three condition functions—constancy of the solubility product, electrical neutrality in the solution, and congruent dissolution of the solid. The equations obtained are

$$\begin{aligned}\ln K_s &= -8403.5/T + 41.863 - 0.09678T \\ \ln K_x &= 51090/T - 341.14 + 0.5880T \\ \ln K_y &= 19373/T - 122.81 + 0.1994T.\end{aligned}$$

The existence of a maximum in K_s in the neighborhood of 25 °C is plausible on the basis of available thermodynamic data for DCPD. Thermodynamic functions are reported for the solution of DCPD and for the association of the ion pairs.

Key words: Calcium phosphate; dicalcium phosphate dihydrate; ion pairs; solubility; solubility isotherms; solubility product.

1. Introduction

In a previous publication [1]¹ on the solubility at 37.5 °C of dicalcium phosphate dihydrate (DCPD), $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$, in dilute phosphoric acid solutions, we reported that the “apparent” solubility product, K'_{DC} , exhibited a concentration dependence. This dependence could be removed by postulating the presence of the ion pairs $[\text{CaHPO}_4^0]$ and $[\text{CaH}_2\text{PO}_4^+]$, making it possible to calculate a “true” solubility product, as well as the stability constants of these ion pairs.

In view of the importance of DCPD in the areas of biology, agronomy and industry, we have extended to other temperatures our solubility measurements of this compound in the ternary system $\text{Ca}(\text{OH})_2 - \text{H}_3\text{PO}_4$

– H_2O to obtain standard free energies, enthalpies and entropies for dissolution of DCPD and for formation of the ion pairs.

We report here the consolidated results and calculations on the solubility behavior of DCPD at 5, 15, 25, and 37.5 °C. Although measurements at 25 °C had been reported previously [2], it was decided to repeat the work at this temperature in order to make all the data comparable in terms of analytical techniques. In the light of our continued experience with these systems we have reevaluated the data collected at 37.5 °C [1] by the use of a more general statistical treatment. No measurements formerly reported [1] have been rejected, but additional measurements have been included.

The data were treated by generalized least squares [3, 4] to obtain estimates of the constants of interest, their standard errors and the adjusted values of the data. The major departure from customary [5, 6] least squares applications introduced in this paper is the use of multicomponent observation and condition function vectors: each of N independent systems is associated with a 4-component observation vector and a 3-component function vector. It will be shown that, where applicable, the imposition of more than one

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**Research Associate of the American Dental Association at the National Bureau of Standards.

***Present address: Forsyth Dental Center, 140 Fenway, Boston, Mass. 02115.

****Director, Research Associate Program of the American Dental Association at the National Bureau of Standards.

¹ Figures in brackets indicate the literature references at the end of this paper.

condition function per system materially reduces the computed standard deviation. We have applied multi-function conditions in other solubility studies [7] and in the study of diffusion in ternary systems [8].

2. Methods and Materials

2.1. Preparation of Materials

Dicalcium phosphate dihydrate and the phosphoric acid solutions were prepared and characterized as described in previous publications [1, 2].

2.2. Experimental Method

The DCPD preparations were leached in a thermostatted saturator with a series of dilute phosphoric acid solutions as described previously [1]. The pH of the effluent was measured in situ and a number of samples (4–8) were collected for the determination of total calcium and phosphorus.

2.3. Calcium and Phosphorus Determinations

Phosphorus was determined spectrophotometrically (relative error, 0.01) in a double beam instrument using the vanado-molybdate reagent of Brabson et al. [9], as described for our previous work at 37.5 °C [1]. Calcium was determined by atomic absorption with a relative error of 0.015.

2.4. pH Determinations

The pH measurements were made with glass and calomel electrodes with a commercially available pH meter (claimed relative accuracy ± 0.0037 pH unit). Standardization of the meter was done with certified NBS buffer standards [10]. The error in the pH measurements was taken as 0.015, which includes the estimated error (0.005) in the value of the standard buffer used [10].

3. Calculations

The aim of these calculations was to obtain as a function of temperature, the "true" solubility product, K_s , of DCPD, the stability constants K_x and K_y , of the ion pairs $[\text{CaHPO}_4]$ and $[\text{CaH}_2\text{PO}_4^+]$, respectively, and the adjusted values of the experimental data. This was accomplished as described, by minimizing the weighted sum of squares of the residuals in the observations subject to three condition functions: saturation with respect to DCPD, electroneutrality, and congruent dissolution of this salt.

Preliminary calculations were done separately on the data collected at each of the four temperatures and the equilibrium constants, K_m , so obtained were each fitted by subsequent adjustments to equations of the form $\ln K_m = A_{m1}T^{-1} + A_{m2} + A_{m3}T$. Since the results of this procedure showed that the assumed form of

temperature dependence was quite reasonable, the calculations reported here were then done on the combined sets of raw data using the above form of temperature dependence ab initio. In this way the nine constants were obtained without the necessity of further adjustment. Throughout this work the temperature was considered as a preset, error-free variable.

In order to formulate the condition functions, it is first necessary to characterize the systems in terms of the measurements and constants. This is done in sections 3.1, 3.2, and 3.3.

3.1. Balance Equations

Using the symbols X^0 and Y^+ for the names and concentrations of the species $[\text{CaHPO}_4^0]$ and $[\text{CaH}_2\text{PO}_4^+]$, respectively, the total molar concentrations of calcium, Ca, and phosphorus, P, are given by

$$\text{Ca} = [\text{Ca}^{++}] + \tau \quad (1)$$

and

$$\text{P} = \sum_{i=0}^3 [\text{H}_i\text{PO}_4^{i-3}] + \tau \quad (2)$$

in which $\tau = X^0 + Y^+$, and $[\text{Ca}^{++}]$ denotes the concentration of free calcium ions. Equation (2) may be written in terms of the activity of the HPO_4^- ion, (HPO_4^-) , and the three dissociation constants k_1 , k_2 , and k_3 of phosphoric acid as

$$\text{P} = (\text{HPO}_4^-) \cdot N + \tau, \quad (3)$$

where

$$N = \sum_{i=0}^3 N_i g_i = \frac{(\text{H}^+)^2}{k_1 k_2} g_0 + \frac{(\text{H}^+)}{k_2} g_1 + g_2 + \frac{k_3}{(\text{H}^+)} g_3. \quad (4)$$

In eq (4), $(\text{H}^+) = 10^{-\text{pH}}$ is hydrogen ion activity and g_i is the reciprocal of the activity coefficient f_i of species i . The subscript i takes the value of the charge magnitude of the several free phosphate species.

3.2. Solubility Product and Concentrations of Ion Pairs

The solubility product is defined here as

$$K_{\text{DC}} = (\text{Ca}^{++}) (\text{HPO}_4^-) = (\text{Ca} - \tau) (\text{P} - \tau) / g_{\text{Ca}} N. \quad (5)$$

In eq (5), and in eqs (6, 7) below, the parentheses around quantities with a charge symbol denote activities. The third member of eq (5) follows from eqs (1) and (3). An apparent solubility product, K'_{DC} , was calculated taking τ to be zero. K_{DC} , as defined by eq (5), is distinct from the quantity K_s ; the latter is the least squares value of the solubility product constant as

found by the adjustment procedure described in section 3.5. The quantity K_{DC} , on the other hand, is the ionic-activity product computed for each individual system; in the absence of experimental errors, its value should be the same for all systems, and equal to K_s , if the saturation condition is fulfilled and if the model for ion pairs is valid.

The concentrations of the ion pairs can be expressed in terms of the stability constants as follows:

$$K_x = (\text{CaHPO}_4^0)/(\text{Ca}^{++})(\text{HPO}_4^-) = X^0/K_{DC}, \quad (6)$$

$$K_y = (\text{CaH}_2\text{PO}_4^+)/(\text{Ca}^{++})(\text{H}_2\text{PO}_4^-) = Y^+/K_{DC}g_1N_1. \quad (7)$$

Adding eqs (6) and (7) and using the identity $\tau = X^0 + Y^+$, a quadratic equation in τ is obtained whose pertinent solution is

$$\tau = U - (U^2 - P \cdot \text{Ca})^{1/2}, \quad (8)$$

where $U = \frac{1}{2}\{P + \text{Ca} + g_{\text{Ca}}N/(K_x + g_1N_1K_y)\}$. Writing $R = (1 + K_x/g_1N_1K_y)^{-1}$, the ion pair concentrations are

$$X^0 = (1 - R)\tau, \quad Y^+ = R\tau. \quad (9)$$

3.3. Ionic Strength and Activity Coefficients

The ionic strength, μ , is defined in these calculations by

$$2\mu = 4(\text{Ca} - \tau) + g_{\text{H}}(\text{H}^+) + g_{\text{OH}}k_w/(\text{H}^+) + Y^+ + \phi_2(P - \tau)/N, \quad (10)$$

where k_w is the dissociation constant of water,

$$\phi_2 = \sum_{i=0}^3 i^2 N_i g_i,$$

and the N_i are defined by eq (4).

Inasmuch as individual ionic activities are required for the computations, the results are bound to reflect the particular expression arbitrarily chosen for the activity coefficients. For this reason calculations were carried through using two different expressions: the Debye-Hückel limiting law extension (D.-H.) and the expression used by Davies [11]. These expressions are given by eqs (11a) and (11b), respectively.

$$-\log f_i = A(T)z_i^2\sqrt{\mu}/(1 + B(T)a_i\sqrt{\mu}) \quad (11a)$$

$$-\log f_i = A(T)z_i^2\{\sqrt{\mu}/(1 + \sqrt{\mu}) - 0.3\mu\} \quad (11b)$$

where z_i is the valence of the i th ion, a_i is the "distance of closest approach" parameter, and A and B are temperature-dependent constants. Following convention, the activity coefficients of the uncharged species H_3PO_4 and $[\text{CaHPO}_4^0]$ were taken as unity. The coefficient of the charged ion pair $[\text{CaH}_2\text{PO}_4^+]$ was taken to be equal to that of the ion H_2PO_4^- .

Values used at the various temperatures for the dissociation constants k_1 , k_2 , k_3 , k_w , and for the parameters $A(T)$ and $B(T)$ are given in table A1, section 6.2. In table A2 are listed the values for the parameters a_i .

Iteration Procedure. Approximate values were first obtained for N in eq (4), and for τ and Y^+ in eqs (8) and (9), using initial guesses for the constants K_x and K_y and assuming all $f_i = 1$. An approximate value of the ionic strength, μ , eq (10), was then obtained which yielded better estimates for the f_i (eq (11)). The calculations were iterated until a constant value of μ was attained (2–3 cycles). New estimates for the parameters A_{mk} were then obtained by the adjustment procedure to be described in 3.5; new values of K_x and K_y computed from eq (16), when inserted into eqs (8) and (9), yielded improved estimates for the ion pair concentrations. A new iteration on μ was started, but using the last values of the f_i , and the whole process was continued until the weighted sum of squared residuals attained a constant value.

3.4. Weights of the Observations

The weights of the observations, defined below by (12), were computed from the estimated variances. The constant s_0 was taken as 1.0×10^{-8} .

$$w = s_0^2/\text{variance} \quad (12)$$

Using the value given in section 2.4 for the error, the variance of pH was calculated as $(0.015)^2$. The variances of phosphorus and of calcium were computed from the relative errors given in section 2.3. At 37.5 °C, the relative error for calcium was 0.025.

3.5. Least Squares Adjustment

This section adheres closely to the notation of section 11.3 of reference [4]. Equation numbers referred to in this text from that source are enclosed in square brackets. The symbols used in this paper are defined in table 1; they differ from those in table [11.3.3] of reference [4] in several respects, as indicated in section 6.1.

TABLE 1. Matrix symbols

Name	Symbol	Order	Element
Condition function.....	f^a	$r \times 1$	$F_q^a(Y_i^a; \beta_v^0)$
Observation.....	y^a	$n \times 1$	Y_i^a
Residual.....	v^a	$n \times 1$	V_i^a
Adjusted observation.....	u^a	$n \times 1$	U_i^a
Weight.....	W^a	$n \times n$	W_{ii}^a (diagonal)
Parameter.....	β	$p \times 1$	$\beta_v = \beta_v^0 - \theta_v$
Correction.....	θ	$p \times 1$	θ_v
	J^a	$r \times p$	$F_{qv}^a = \partial F_q^a / \partial \beta_v$
	F^a	$r \times n$	$F_{qi}^a = \partial F_q^a / \partial Y_i^a$
	L^a	$r \times r$	$L_{qs}^a = \sum_i F_{qi}^a F_{si}^a W_{ii}^{a-1}$
Lagrangian.....	λ^a	$r \times 1$	λ_q^a
	C	$p \times p$	$C_{\mu\nu}$

The general formulation of reference [4], applied to the combined data (35 points) with 3 condition functions per system and 9 parameters, leads to the matrix [11.3.3, 1a] of order $3 \times 35 + 9 = 114$. In an alternative formulation of the normal equations [11.3.3.1, 5a], the matrix L is of order $3 \times 35 = 105$. However, if the condition functions for the α th system depend on the measurements on that system only, as is true here, then, as shown in section 3.5.3, the order of the largest matrix that appears is 9, the maximum number of parameters considered here.

a. Condition Functions

The available conditions to be imposed on each system are:

1. F_1^α : Saturation with respect to DCPD

$$(Ca - \tau)(P - \tau)/g_{Ca}N - K_s = 0. \quad (13)$$

2. F_2^α : Electroneutrality

$$2(Ca - \tau) + g_H(H^+) + Y^+ - g_{OH}k_w/(H^+) - \phi_1(P - \tau)/N = 0, \quad (14)$$

where $\phi_1 = \sum_{i=1}^3 iN_i g_i$.

3. F_3^α : Congruent dissolution of DCPD

$$Ca/(P - P_0) - 1 = 0, \quad (15)$$

where P_0 is the molar concentration of initial phosphoric acid.

In eq (13), K_s is the solubility product constant to be estimated. The stability constants to be estimated, K_x and K_y , appear implicitly in τ and Y^+ ; see eqs (8) and (9).

b. Choice of Parameter and Indices

In these calculations the equilibrium constants were represented by equations of the form

$$\ln K_m = \sum_{k=1}^L A_{mk} T^{k-2}, \quad \begin{cases} L = 1 \text{ or } 3 \\ m = 1, \dots, C \end{cases} \quad (16)$$

where $m = 1, 2, 3$ corresponds to the subscripts s, x and y , and T is the temperature in kelvins. In the case $L = 1$ (computations at individual temperatures), T^{-1} was replaced by 1 . The number of constants, C , was 3 in every case except when ion pairs were assumed absent. In any event, $p = CL$ is the total number of parameters, A_{mk} , to be found, and $\beta = (A_{11}, \dots, A_{1L}, \dots, A_{CL})$.

In order to establish the soundness of the data treatment adopted here, i.e., assumption of the presence of ion pairs and use of three condition functions, calculations were made using the following combinations of parameters and functions: (I) Calculations at individual temperatures, assuming ion pairs present; (II) combined data at all temperatures, with

temperature dependence for K_s , but ion pairs assumed absent; (III) combined data, ion pairs present, and temperature dependence of the K_m . In each of these cases, separate calculations were made, using as conditions: (A) F_1^α only; (B) F_1^α and F_2^α ; (C) F_1^α, F_2^α , and F_3^α . (When F_3^α is omitted, the observable P_0 is not used, i.e., $n = 3$). These combinations are tabulated below. The calculated quantities reported here correspond to Case III-C.

Case	C	L	p	r	n
I	3	1	3	3	4
II-A	1	3	3	1	3
-B				2	4
-C				3	4
III-A	3	3	9	1	3
-B				2	4
-C				3	4

c. Reduced Normal Equations and Their Solution

In terms of the analysis of this paper, the reduced or "p normal" [12] eqs [11.3.3.1, 5a], may be written

$$C\theta = z, \quad (17)$$

where

$$C = \sum_{\alpha} \tilde{J}^{\alpha} L^{\alpha-1} J^{\alpha}, \quad z = \sum_{\alpha} \tilde{J}^{\alpha} L^{\alpha-1} f^{\alpha}. \quad (18)$$

Since J^{α} is of order $r \times p$ and L^{α} is of order $r \times r$, the matrix C is of order $p \times p$.

Equation (17) was scaled by the substitution $\theta = D^{-1}\theta^*$ and premultiplication by D^{-1} to give

$$C^*\theta^* = z^*, \quad (19)$$

where $D_{\nu\nu'} = \sqrt{C_{\nu\nu}}\delta_{\nu\nu'}$ ($\delta_{\nu\nu'}$ is the Kronecker delta), $C^* = D^{-1}CD^{-1}$, and $z^* = D^{-1}z$. The solution for the parameter corrections is then

$$\theta = D^{-1}C^{*-1}z^*. \quad (20)$$

The inversion of C^* was accomplished using Gaussian elimination and double precision arithmetic.

New estimates, $\beta = \beta^0 - \theta$, were thus obtained and used for a subsequent iteration (sec. 3.3).

The convergence of the process at the n th iteration was followed by computing the sum of squares (q^2) and testing the ratio q_n^2/q_{n-1}^2 against 10^{-7} . For $p = 3$, convergence was attained in 3-4 cycles and for $p = 9$, about 15 cycles were required. The expression used for q^2 is given in eq (A-15) of section 6.1c. In computations for consecutive values of α during a given cycle, partial sums (denoted by the prime) were accumulated:

$$C'_{(\alpha)} = C'_{(\alpha-1)} + J^{\alpha} L^{\alpha-1} J^{\alpha},$$

$$z'_{(\alpha)} = z'_{(\alpha-1)} + J^{\alpha} L^{\alpha-1} f^{\alpha},$$

and

$$q_{(\alpha)}^{2'} = q_{(\alpha-1)}^{2'} + \tilde{f}^{\alpha} L^{\alpha-1} f^{\alpha}.$$

The sum $q_{(N)}^{2'} = \sum_{\alpha} \tilde{f}^{\alpha} L^{\alpha-1} f^{\alpha}$ was then corrected, after obtaining the solution for θ , by subtracting the quantity $\theta C \theta$.

d. Standard Deviation and Errors

The total number of condition functions considered here is Nr , i.e., the number of systems, times the number of functions per system. Hence, [11.3.4.1, 3] for the estimated sum of squares is

$$\mathcal{E}(\sum_{\alpha} \tilde{V}^{\alpha} W^{\alpha} V^{\alpha}) = (Nr - p) s^2. \quad (21)$$

The standard deviation of the adjustment is thus

$$s = \sqrt{[q^2 / (Nr - p)]}, \quad (22)$$

with dispersion (standard error) given by [13]

$$\sigma\{s\} = s / \sqrt{[2(Nr - p)]}.$$

The covariance matrix of the parameter set β is $s^2 C^{-1}$ by [11.3.4.2c] and (A-1). This may be written as

$$\text{Cov } \beta = s^2 [(C^{-1})_{mm'}], \quad m, m' = 1, \dots, C. \quad (23)$$

Here $s^2 (C^{-1})_{mm'}$, one of the C^2 submatrices of $s^2 C^{-1}$, is of order $L \times L$ and is the moment matrix of the set $(A_{mk}, A_{m'k'})$. (See eq (16)). Then the elements of the covariance matrix for the pair of equilibrium constants $K_m, K_{m'}$ are given by

$$\text{Cov } (K_m, K_{m'}) = s^2 K_m \tilde{\chi}_t (C^{-1})_{mm'} \chi_t K_{m'}, \quad (24)$$

where the vector $\tilde{\chi}_t = (1)$ for $L = 1$, and $\tilde{\chi}_t = (T_t^{-1}, 1, T_t)$ for $L = 3$. When the selected temperatures are identical ($t = t'$), the dispersion of K_m is given by

$$\sigma\{K_m\} = \sqrt{[\text{Cov } (K_m, K_m)]}. \quad (25)$$

For the adjusted observations the dispersions were computed from eq (A-10) by

$$\sigma\{U_i^g\} = \sqrt{[\text{cov } (U_i^g, U_i^g)]}. \quad (26)$$

4. Results

4.1. Solubility and Solubility Products

The compositions of saturated DCPD solutions at four temperatures are summarized in tables 2 through 5. Congruent dissolution of the salt is indicated by the

Table 2. Solubility of DCPD at 5 °C

Unadjusted quantities

Initial acid, P ₀ <i>M</i> × 10 ³	Composition of equil. solns.			Ca P - P ₀	<i>K'</i> _{DC} × 10 ⁷	
	pH	Ca <i>M</i> × 10 ³	P <i>M</i> × 10 ³		Davies	D.-H.
0.0979	7.64 ₂	0.755	0.843	1.01	2.96	2.98
.490	6.87 ₈	1.00	1.49	1.00	2.95	2.97
.987	6.40 ₀	1.41	2.44	0.969	2.74	2.77
2.94	5.66 ₈	3.18	6.12	.999	2.81	2.86
4.83	5.25 ₅	5.13	9.92	1.01	2.60	2.66
9.78	4.73 ₈	9.95	19.6	1.01	2.53	2.63
10.1	4.71 ₃	10.3	20.4	1.00	2.56	2.66
19.7	4.27 ₅	19.6	39.3	0.999	2.75	2.90
49.5	3.72 ₀	47.2	96.8	0.997	3.33	3.46

TABLE 3. Solubility of DCPD at 15 °C

Unadjusted quantities

Initial acid, P ₀ <i>M</i> × 10 ³	Composition of equil. solns.			Ca P - P ₀	<i>K'</i> _{DC} × 10 ⁷	
	pH	Ca <i>M</i> × 10 ³	P <i>M</i> × 10 ³		Davies	D.-H.
0.0967	7.62 ₇	0.736	0.842	0.988	2.93	2.95
.499	6.79 ₃	1.01	1.51	.998	2.83	2.86
1.01	6.36 ₆	1.41	2.41	1.01	2.78	2.81
2.95	5.60 ₆	3.20	6.03	1.04	2.69	2.74
4.83	5.20 ₉	5.11	9.96	0.996	2.59	2.66
5.04	5.17 ₅	5.19	10.1	1.02	2.47	2.54
10.0	4.68 ₀	9.97	19.8	1.02	2.48	2.58
20.1	4.21 ₅	19.4	39.0	1.02	2.61	2.75
50.0	3.62 ₈	46.7	96.4	1.01	2.89	3.01

TABLE 4. Solubility of DCPD at 25 °C

Unadjusted quantities

Initial acid, P ₀ <i>M</i> × 10 ³	Composition of equil. solns.			Ca P - P ₀	<i>K'</i> _{DC} × 10 ⁷	
	pH	Ca <i>M</i> × 10 ³	P <i>M</i> × 10 ³		Davies	D.-H.
0.101	7.58 ₀	0.760	0.847	1.02	2.98	3.00
.503	6.77 ₅	1.03	1.49	1.05	2.89	2.92
1.02	6.33 ₀	1.41	2.42	1.00	2.75	2.78
2.98	5.58 ₃	3.27	6.21	1.01	2.84	2.90
4.91	5.18 ₄	5.19	10.2	0.978	2.70	2.78
9.70	4.72 ₈	10.1	19.9	.985	2.98	3.10
19.7	4.22 ₁	19.7	39.1	1.01	2.84	3.00
49.5	3.65 ₂	47.2	97.6	.983	3.29	3.44

values of the Ca : (P - P₀) ratio, which do not depart significantly from unity. In columns 6 and 7 are given the apparent solubility products, *K'*_{DC}, (assuming no ion pairs) of the salt calculated with the use of the activity coefficients of Davies and of Debye-Hückel, respectively. It is apparent that the results exhibit the trend noted in previous work [1]: a minimum value of

TABLE 5. Solubility of DCPD at 37.5 °C

Unadjusted quantities

Initial acid, P_0 $M \times 10^3$	Composition of equil. solns.			$\frac{Ca}{P-P_0}$	$K'_{DC} \times 10^7$	
	pH	Ca $M \times 10^3$	P $M \times 10^3$		Davies	D.-H.
0.498	6.75 ₅	1.02	1.50	1.02	2.84	2.86
1.00	6.30 ₅	1.41	2.40	1.01	2.66	2.69
1.00	6.29 ₉	1.37	2.43	0.963	2.60	2.63
5.02	5.13 ₂	5.29	10.1	1.04	2.47	2.55
5.02	5.12 ₀	5.32	10.2	1.04	2.43	2.50
9.99	4.58 ₇	10.5	20.3	1.01	2.31	2.42
20.2	4.13 ₇	19.7	40.3	.980	2.43	2.58
20.2	4.13 ₀	20.2	40.4	1.00	2.43	2.59
49.8	3.56 ₀	48.9	97.9	1.02	2.73	2.87

K'_{DC} occurs near a pH of 5. The K'_{DC} values in columns 6 and 7 tend to converge in the more dilute solutions, since both expressions for ionic activity coefficients approach the limiting law in this region.

Tables 6 through 9 summarize the data adjustments for 5, 15, 25, and 37.5 °C, respectively, as obtained under the conditions of Case III-C in section 3.5b

TABLE 6. Solubility of DCPD at 5 °C

Adjusted quantities

Initial acid, P_0 $M \times 10^3$	Composition of equil. solns.			$\frac{Ca}{P-P_0}$	$\mu \times 10^3$	$K_{DC} \times 10^7$
	pH	Ca $M \times 10^3$	P $M \times 10^3$			
0.0984	7.66 ₁	0.753	0.851	1.00	2.49	2.33 ₈
.482	6.84 ₄	1.00	1.49	1.00	3.10	2.33 ₉
.996	6.39 ₁	1.41	2.40	1.00	4.18	2.33 ₉
2.91	5.62 ₇	3.18	6.10	1.00	9.17	2.34 ₈
4.85	5.25 ₁	5.07	9.92	1.00	14.5	2.33 ₉
9.78	4.75 ₁	9.92	19.7	1.00	27.7	2.33 ₉
10.1	4.72 ₆	10.3	20.4	1.00	28.6	2.33 ₉
19.7	4.27 ₆	19.6	39.3	1.00	52.8	2.33 ₈
49.2	3.70 ₃	47.6	96.8	1.00	119.	2.34 ₀

TABLE 7. Solubility of DCPD at 15 °C

Adjusted quantities

Initial acid, P_0 $M \times 10^3$	Composition of equil. solns.			$\frac{Ca}{P-P_0}$	$\mu \times 10^3$	$K_{DC} \times 10^7$
	pH	Ca $M \times 10^3$	P $M \times 10^3$			
0.0969	7.63 ₆	0.746	0.843	1.00	2.61	2.53 ₅
.502	6.79 ₅	1.01	1.51	1.00	3.25	2.53 ₅
1.01	6.35 ₉	1.41	2.42	1.00	4.32	2.53 ₅
2.93	5.60 ₀	3.17	6.10	1.00	9.33	2.53 ₅
4.88	5.22 ₁	5.07	9.94	1.00	14.7	2.53 ₅
5.03	5.20 ₃	5.21	10.2	1.00	15.2	2.54 ₁
9.98	4.70 ₀	10.1	20.0	1.00	28.8	2.54 ₃
19.8	4.23 ₆	19.7	39.5	1.00	54.8	2.54 ₀
49.6	3.65 ₀	47.5	97.1	1.00	126.	2.54 ₁

TABLE 8. Solubility of DCPD at 25 °C

Adjusted quantities

Initial acid, P_0 $M \times 10^3$	Composition of equil. solns.			$\frac{Ca}{P-P_0}$	$\mu \times 10^3$	$K_{DC} \times 10^7$
	pH	Ca $M \times 10^3$	P $M \times 10^3$			
0.101	7.58 ₄	0.751	0.852	1.00	2.64	2.56 ₁
.499	6.76 ₈	1.01	1.51	1.00	3.27	2.56 ₁
1.01	6.32 ₅	1.41	2.43	1.00	4.36	2.56 ₁
2.98	5.55 ₈	3.22	6.20	1.00	9.52	2.56 ₇
4.97	5.17 ₉	5.15	10.1	1.00	15.1	2.56 ₂
9.79	4.69 ₀	9.88	19.7	1.00	28.6	2.57 ₈
19.7	4.20 ₄	19.5	39.2	1.00	55.2	2.56 ₄
49.5	3.61 ₃	47.1	96.6	1.00	128.	2.57 ₃

TABLE 9. Solubility of DCPD at 37.5 °C

Adjusted quantities

Initial acid, P_0 $M \times 10^3$	Composition of equil. solns.			$\frac{Ca}{P-P_0}$	$\mu \times 10^3$	$K_{DC} \times 10^7$
	pH	Ca $M \times 10^3$	P $M \times 10^3$			
0.492	6.73 ₇	1.01	1.51	1.00	3.18	2.37 ₅
.995	6.29 ₇	1.41	2.40	1.00	4.25	2.37 ₅
1.00	6.29 ₂	1.42	2.42	1.00	4.26	2.37 ₄
5.00	5.13 ₁	5.20	10.2	1.00	15.2	2.37 ₄
5.02	5.12 ₈	5.22	10.2	1.00	15.2	2.37 ₄
10.1	4.62 ₁	10.2	20.3	1.00	29.6	2.37 ₈
20.3	4.14 ₂	20.0	40.3	1.00	56.9	2.37 ₅
20.3	4.14 ₀	20.0	40.4	1.00	57.1	2.37 ₅
50.3	3.56 ₃	47.2	97.5	1.00	130.	2.37 ₄

using D.-H. activity coefficients. Comparison with tables 2 through 5 shows that in all systems the magnitudes of the individual residuals are small relative to the values of the corresponding observables. The small size of the relative adjustments, (residual/observed value) $\times 100$, is crucial, since the linearization of the condition functions, neglecting higher order terms, can be justified only if the above ratios are indeed small.

The relative dispersion of the adjusted values of Ca and P, $\sigma\{U_i^q\}/U_i^q$, where the dispersions are given by eq (26), are not shown in the tables, but were well below the assigned relative errors given in section 2.3; likewise, the dispersion of the adjusted pH values were less than the absolute error given in section 2.4. Thus, the calculated dispersions support the reasonableness of the weights assigned in section 3.4.

The last two columns of tables 6 to 9 give the ionic strength and solubility product, K_{DC} , calculated with the adjusted data and final values of the stability constants. The values of K_{DC} are given with more figures than are significant to indicate the adequacy of the adjustment procedure. Since K_{DC} is defined (sec. 3.2) as the function $(Ca - \tau)(P - \tau)/g_{Ca}N$, its near invariance over the range of concentrations supports the correctness of the model involving two ion pairs.

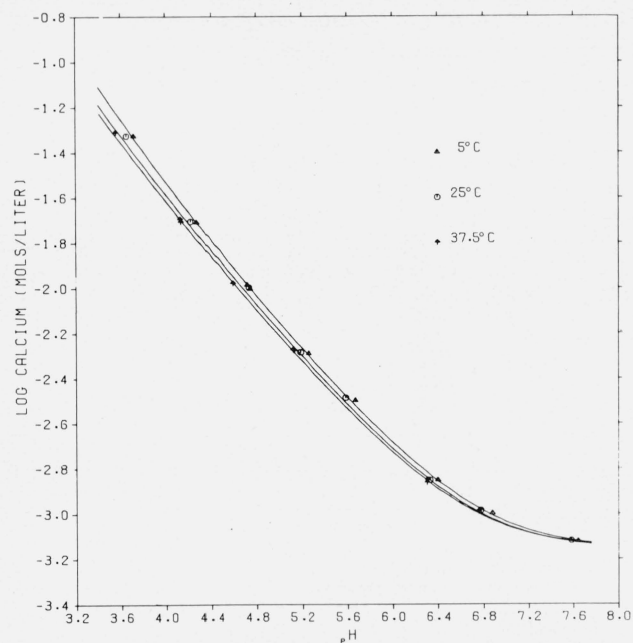


FIGURE 1. Calculated solubility isotherms of DCPD at 5, 25, and 37.5°C.

Points represent experimental data.

In this respect it may be observed that the variations in the listed K_{DC} values are clearly independent of pH, in contrast with those for K'_{DC} in tables 2 to 5. Finally, it may be observed that the K_{DC} values are practically identical to the value of the solubility parameter K_s listed in table 12. This is further evidence as to the soundness of the adjustment and the applicability of the model.

4.2. Solubility Isotherms

In figure 1 are shown the solubility isotherms for DCPD in terms of total concentration of calcium as a function of pH for three temperatures. These curves were computed, as explained in section 5.1, on the basis of the constants derived here. Thus, these curves are the loci of the adjusted data. Experimental points are shown on the same plot. It is apparent that the experimental data at 5 and 37.5°C are well represented by the calculated isotherms. The reason for the less satisfactory fit for the data at 25°C will be discussed in section 5.1. The isotherm for 15°C lies very close to that for 25°C and, for the sake of clarity, is not shown. The relative positions of the isotherms in figure 1, show that the solubility of DCPD decreases with increase in temperature. This behavior is similar to that displayed [14] by CaHPO_4 although the decrease in solubility is more marked in the latter case. Similarly smooth curves are obtained if the concentration of phosphorus is plotted against pH or if the concentration of calcium is plotted against the concentration of phosphorus.

4.3. Ion pairs

The concentration of the ion pair $[\text{CaH}_2\text{PO}_4^+]$, Y^+ , and the percent of bound calcium ($100 \tau/\text{Ca}$) for the adjusted data are given for all systems in tables 10 and 11. In table 10 the results for 25°C are shown for the calculations using the Davies and the D.-H. ionic activity coefficients. Only the results obtained with the latter coefficients are given in table 11 for the other three temperatures, since, as indicated by the values in table 10, the results using the two types of coefficients do not differ markedly. The concentration of the ion pair $[\text{CaHPO}_4^0]$, X^0 , was nearly invariant in all systems at each temperature, its value being calculated in each cycle from eq (9), involving the quantities R and τ , both of which vary with pH. This constancy was not assumed ab initio but is a consequence of saturation: eq (6) gives $X^0 = K_x \cdot K_{DC}$ and therefore X^0 should be constant under the condition of saturation with respect to DCPD. The values of X^0 and its dispersion, given at the foot of each table, were computed after the final cycle, with K_s replacing K_{DC} in eq (6).

4.4. Equilibrium Constants

In table 12 are assembled the parameters A_{mk} of eq (16) and the sets of values of K_s , K_x , and K_y , and their respective errors at each of the four temperatures. (The standard deviation is discussed in section 5a.) The values obtained using the D.-H. and the Davies activity coefficients are both shown. The differences in the values so obtained persists in a uniform manner from one temperature to another. Values of K_s , K_x , and K_y , given by eq (16), are plotted in figure 2; their standard errors are indicated at the four experimental temperatures. The presence of a minimum in K_x is in agreement with the behavior observed in many other weak electrolytes; usually they exhibit ionization maxima in the region 0 to 60°C and it has been suggested [15] that this is a property of all weak electrolytes. It is noteworthy that such a maximum (minimum for association) has been reported [16] for the second ionization constant of phosphoric acid. Furthermore, the maximum in K_s can be antici-

TABLE 10. Concentrations of ion pairs and bound calcium at 25°C

Debye-Hückel			Davies		
pH	$Y^+, M \times 10^3$	$100 \tau/\text{Ca}$	pH	$Y^+, M \times 10^3$	$100 \tau/\text{Ca}$
7.58 ₄	0.0006	8.76	7.58 ₃	0.0004	8.96
6.76 ₈	.0037	6.83	6.76 ₇	.0025	6.89
6.32 ₅	.0104	5.35	6.32 ₄	.0069	5.26
5.55 ₈	.0631	3.99	5.55 ₈	.0405	3.47
5.17 ₉	.154	4.25	5.18 ₁	.0964	3.41
4.69 ₀	.496	5.68	4.69 ₄	.297	4.21
4.20 ₄	1.59	8.48	4.20 ₉	.905	6.05
3.61 ₃	6.70	14.4	3.60 ₈	4.75	10.2
$X^0 = 0.0652 \pm 0.0080$			$X^0 = 0.0669 \pm 0.0081$		

TABLE 11. Concentrations of ion pairs and bound calcium calculated with D.-H. activity coefficients ^a

5 °C			15 °C			37.5 °C		
pH	Y ⁺ , M × 10 ³	100 τ/Ca	pH	Y ⁺ , M × 10 ³	100 τ/Ca	pH	Y ⁺ , M × 10 ³	100 τ/Ca
7.66 ₁	0.0010	14.0	7.63 ₆	0.0007	9.34	6.73 ₇	0.0032	9.72
6.84 ₄	.0069	11.1	6.79 ₅	.0049	7.31	6.29 ₇	.0088	7.39
6.39 ₁	.0197	8.80	6.35 ₉	.0134	5.85	6.29 ₂	.0089	7.36
5.62 ₇	.118	7.00	5.60 ₀	.0792	4.67	5.13 ₁	.137	4.46
5.25 ₁	.285	7.68	5.22 ₄	.193	5.16	5.12 ₈	.138	4.46
4.75 ₁	.937	10.5	5.20 ₃	.203	5.22	4.62 ₁	.462	5.45
4.72 ₆	.995	10.7	4.70 ₉	.658	7.22	4.14 ₂	1.46	7.78
4.27 ₆	2.92	15.4	4.23 ₆	2.05	10.8	4.14 ₀	1.47	7.79
3.70 ₃	11.7	24.9	3.65 ₀	8.49	18.0	3.56 ₃	5.97	12.8
X° = 0.104 ± 0.010			X° = 0.0690 ± 0.0079			X° = 0.0954 ± 0.0153		

^a The values are not comparable across the table due to differences in initial H₃PO₄ concentrations.

TABLE 12. Temperature dependence of equilibrium constants

$\ln K_m = \sum_{k=1}^{k=3} A_{mk} T^{-2+k} \text{ [eq (16)]}$								
Debye-Hückel					Davies			
A_{mk}					A_{mk}			
$m \backslash k$	1	2	3		1	2	3	
1(s).....	-8403.5	41.863	-0.096779		-9418.4	48.746	-0.10848	
2(x).....	51090	-341.14	.58804		54735	-365.90	.63022	
3(y).....	19373	-122.81	.19943		31465	-202.88	.33085	
$K_m \backslash \text{°C}$	5	15	25	37.5	5	15	25	37.5
$K_s \times 10^7$	2.33 ₈ ± 0.058	2.53 ₅ ± 0.044	2.56 ₁ ± 0.048	2.37 ₅ ± 0.057	2.28 ₉ ± 0.058	2.50 ₅ ± 0.044	2.53 ₄ ± 0.048	2.32 ₈ ± 0.057
K_x	446 ± 54	272 ± 35	255 ± 35	401 ± 71	479 ± 57	283 ± 36	264 ± 36	431 ± 74
K_y	10.1 ± 1.7	6.62 ± 1.23	5.10 ± 1.03	4.51 ± 1.44	9.69 ± 1.83	5.23 ± 1.29	3.67 ± 0.98	3.28 ± 1.48

pated, as shown in section 5a, on the basis of the thermodynamic properties of DCPD itself.

4.5. Thermodynamic Quantities

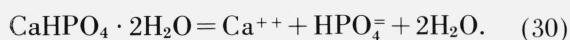
The results of the thermodynamic computations are given in table 13. The values of the thermodynamic functions were calculated from eq (16) and the following equations:

$$\Delta G^0 = -RT \ln K_m = -R(A_{m1} + A_{m2}T + A_{m3}T^2), \quad (27)$$

$$\Delta S^0 = -(\partial \Delta G^0 / \partial T) = R(A_{m2} + 2A_{m3}T), \quad (28)$$

$$\Delta H^0 = \Delta G^0 + T\Delta S^0 = R(-A_{m1} + A_{m3}T^2), \quad (29)$$

where R is the gas constant. For DCPD ($m=1$) the functions refer to the dissolution of 1 mole of CaHPO₄ · 2H₂O according to the reaction



In the case of the ion pairs, [CaHPO₄⁰] ($m=2$) and [CaH₂PO₄⁺] ($m=3$), each function applies to the formation of 1 mole of the ion pair from its constituent calcium and ortho-phosphate ions. The errors were computed by use of the appropriate moment matrix of the A_{mk} , eq (23), and the derivatives of eqs (27–29). Whereas the errors for the quantities associated with the dissolution of DCPD, and formation of [CaHPO₄⁰] are within acceptable limits, this is not the case for those related to the formation of [CaH₂PO₄⁺].

The negative values of ΔS^0 for formation of the ion pairs at the lower temperatures are atypical. It would be desirable to check these values by another experimental method. On the other hand, the value of ΔS_{25}^0 , -31.5 ± 0.8 cal/mol.deg, for eq (30) is in satisfactory agreement with the value -32.56 calculated from the S^0 (DCPD) [21] and the entropies [22]² of the products in that equation.

² The revised value of -12.7 cal/mol deg for S_{25}^0 (Ca⁺⁺) was supplied by Dr. V. B. Parker, Thermochemistry Section, NBS.

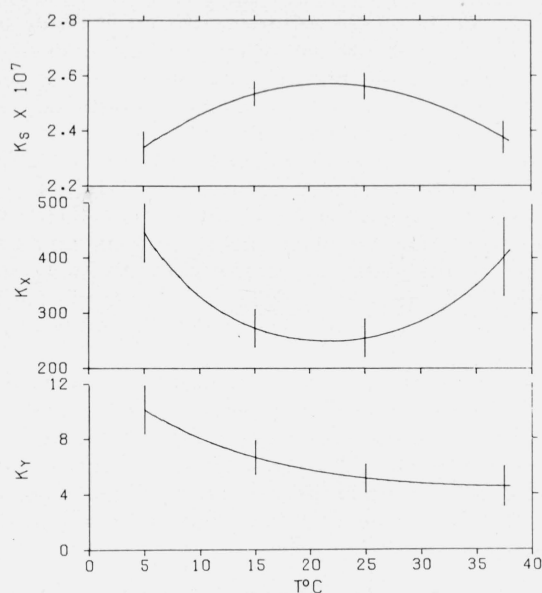


FIGURE 2. Temperature dependence (eq (16)) of the solubility product of DCPD and the stability constants for ion pairs.

Length of vertical lines at the four experimental temperatures corresponds to twice the standard errors.

It may be observed that the thermodynamic values appear to be relatively insensitive to the choice of activity-coefficient expression, and that the two sets of values differ by less than their errors. (The errors are approximately the same for the two sets.) By way of contrast, the large temperature dependence of the equilibrium constants produces marked variations in ΔH° and ΔS° ; this is so for the values pertaining to the dissolution process even though the temperature coefficient of K_s is relatively small. It is clear that a high degree of confidence in the results can be attained only by measurements made at short temperature intervals and extended over the widest practical temperature range. Thus, measurements on DCPD at other temperatures are highly desirable.

5. Discussion

5.1. Solubility isotherms

The measurements reported in this paper were made on solutions that had reached equilibrium with respect to DCPD from undersaturation; the experimental design was selected on the basis of previous experience [1, 2] to assure attainment of equilibrium conditions. The consistency of the data, the smooth-

TABLE 13. Thermodynamic quantities

t °C	Dissolution of DCPD			Formation of $[\text{CaHPO}_4]$			Formation of $[\text{CaH}_2\text{PO}_4^+]$		
	ΔG° kJ/mol	ΔH° kJ/mol	ΔS° J/mol.K	ΔG° kJ/mol	ΔH° kJ/mol	ΔS° J/mol.K	ΔG° kJ/mol	ΔH° kJ/mol	ΔS° J/mol.K
5	35.3 ± 0.04 ^b 35.3	7.6 ± 2.5 8.5	-99.6 ± 8.8 -96.6	-14.1 ± 0.3 -14.3	-46 ± 15 -50	-117 ± 54 -125	-5.4 ± 0.4 -5.3	-33 ± 22 -50	-100 ± 79 -155
15	36.4 ± 0.04 36.4	3.0 ± 1.2 3.4	-115 ± 4 -115	-13.4 ± 0.3 -13.5	-19 ± 7 -20	-19 ± 24 -23	-4.5 ± 0.5 -4.0	-23 ± 10 -33	-67 ± 34 -100
25	37.6 ± 0.04 37.7	-1.7 ± 1.0 -1.9	-132 ± 3 -133	-13.7 ± 0.3 -13.8	10 ± 7 11	79 ± 23 84	-4.1 ± 0.5 -3.2	-14 ± 12 -17	-32 ± 40 -46
37.5	39.4 ± 0.04 39.4	-7.8 ± 2.6 -8.7	-152 ± 9 -155	-15.5 ± 0.5 -15.7	46 ± 19 50	201 ± 63 213	-3.9 ± 0.8 -3.0	-1 ± 30 4	9 ± 100 23

^a D.-H. activity coefficients. ^b Davies activity coefficients.

ness of the experimental plots, and the success of the adjustment procedure in the calculation of a solubility product constant applicable to all the systems (over a wide range of solution compositions) constitute further evidence that a true equilibrium was attained in the experiments reported here. The adjustment of the data yields points which lie on the calculated isotherms at the several temperatures (fig. 1), and it may be seen from tables 2-9 that the only residuals that exceed 2 percent of the observed value are those of calcium, one at 25 and two at 37.5 °C. Furthermore, the residuals of positive sign constitute approximately half of the total at each temperature.

The discrepancy at low pH values between the data at 25 °C and the isotherm computed for that temperature can be attributed to the difference between two estimates of the value of K_y . The adjustment of these data alone (Case I, sec. 3.5b) resulted in values for K_s , K_x , and K_y of 2.59×10^{-7} , 244, and 8.2, respectively. Isotherms computed with these values, and with the values reported for K_s and K_x (table 12) but with 8.2 for K_y , both fitted the data in a satisfactory manner. Nevertheless, we have elected to accept the lower estimate (5.1) of the value of K_y for the sake of increased confidence in the values of K_s and K_x resulting from the adjustment of the combined data.

Thus, the curves in figure 1 constitute solubility isotherms for DCPD at the indicated temperatures; they represent solutions metastable with respect to CaHPO_4 [14] over all the experimental range, and with respect to hydroxyapatite [1], β -tricalcium phosphate [17], and octacalcium phosphate [18] in parts of that range. Metastability, however, does not preclude the application of thermodynamic concepts to these systems so long as precipitation of more insoluble calcium phosphates is impossible to detect during the time of the experiment. In this connection, if more basic calcium phosphates had precipitated, the apparent $\text{Ca}:(\text{P}-\text{P}_0)$ ratio for the dissolution reaction would be significantly less than unity; the ratios reported here do not depart significantly from unity. For example, at 25 °C, table 4, the dissolution ratios may be weighted by propagation on the quantity $\text{Ca}:(\text{P}-\text{P}_0)$. The weighted average ratio obtained is 1.0067 with standard error of the mean 0.0087. With 7 degrees of freedom, the excess over unity of the average ratio would have to exceed 0.020 to be significant at the 95 percent confidence level. Similar conclusions can be drawn from the data at other temperatures. Furthermore, with one exception [1], petrographic examination of the solid phase after the saturated solution was obtained failed to show any solid other than DCPD.

Effect of Temperature on the Solubility of DCPD. Examination of the curves in figure 1 leads to the tentative conclusion that the solubility of DCPD varies inversely with temperature. However, since the observed solubility differences are very small, it was considered desirable to ascertain the significance of these differences by the following statistical procedure. The isotherms in figure 1 were generated, using the constants K_x , K_y , and K_s as found by the adjustment procedure (D.-H. activity coefficients), by solving the electroneutrality eq (14) for calcium concentrations corresponding to a selected set of pH values. The value for total phosphorus used in this equation, as well as the derivatives of calcium with respect to the three equilibrium constants, were obtained from the saturation condition, eq (13). The variance of calcium was calculated at each pH by use of the derivatives and the covariance matrix, eq (24), of the constants as given by the adjustment. For two temperatures, $T_1 < T_2$, $\text{Ca}(T_1)$ was compared with $\text{Ca}(T_2)$ at the 95 percent level by direct computation of critical values [19].

The results indicated, with one exception, that throughout the larger part (4.0–6.4) of the experimental pH range, the solubility of DCPD decreased significantly with increase in temperature. The exception to this statement is that there was no significant difference between the solubility at 15 and at 25 °C. The resulting plateau can be related to the variation of the equilibrium constants with temperature shown in figure 2. Between 5 °C and a temperature near 25 °C, the decrease in K_x should tend to depress the solubility of DCPD, whereas from that temperature up to 37 °C the reverse effect would be expected. The temperature variation of K_s clearly should have the

opposite effects on the solubility over the range 5 to 37 °C. Thus, in the region where the extrema in the curves occur, a decreasing rate of change of solubility with temperature should be anticipated. The results, therefore, indicate that the decrease in the relative concentration of ion pairs (tables 10–11) is a dominant factor in the decrease of the solubility of DCPD in the region 5 to about 25 °C. Above this temperature, the dominant factor appears to be the decrease in the value of K_s . The decrease in K_y over the whole temperature range would reinforce the effect of K_x in the lower, and that of K_s in the upper, region.

It is noteworthy that the anhydrous salt [14] does not display any solubility plateau, which possibly is due to the monotonic decrease of K_s with temperature for that compound. The variation of K_s with temperature for both compounds can be anticipated on the basis of their respective thermodynamic properties, as discussed in section 5.2a.

5.2. Equilibrium Constants

a. Dependence Upon Conditions and Hypotheses

The solubility product constant, K_s , obtained by the adjustment procedure is a least-squares estimate and is thus associated with a minimum sum of squares, i.e., eq (A-15). With a given set of data, however, the actual value of q^2 at the minimum, as well as the value of K_s itself, depend upon the condition functions that are satisfied by the systems and upon the hypothesis of ion pairs. This is illustrated in table 14. Because the number of condition functions and parameters vary across the columns of the table, the results are best compared by reference to the sixth line, which gives the standard deviation of the adjustment, eq. (22).

It is clear from the table that the use of three condition functions has definite advantages over the use of only one condition function, whether ion-pairs are considered or not. Furthermore, it is evident that the minimum value of the standard deviation is obtained by the use of three condition functions with the hypothesis of ion pairs present. Thus, the best set of values for K_s , K_x , and K_y are those obtained with the use of three condition functions. The argument for the presence of ion pairs is strengthened by this comparison. In a previous publication [1] we reported a set of values for K_s , K_x , and K_y at 37.5 °C which differ from those reported here. Although the present calculations are based on a larger sample of data, these differences are primarily due to the method of calculation. The criteria used in our earlier work [1] were valid but the procedure to establish an unequivocal minimum in the standard variance was not fully adequate. Treatment of the previously published data [1] by the adjustment procedure of the present paper yielded results in agreement with the values reported in table 12.

b. Temperature Dependence of K_s

The appearance of a maximum in the K_s of DCPD in the neighborhood of 25 °C, as shown in figure 2, de-

TABLE 14. Effect of the number of condition functions and the ion pair hypothesis on the estimates of the standard deviation and the equilibrium constants

Function(s) ^a	1		1 + 2		1 + 2 + 3	
Case ^b	II-A	III-A	II-B	III-B	II-C	III-C
Ion pairs.....	Absent	Present	Absent	Present	Absent	Present
Degrees of freedom.....	32	26	67	61	102	96
$q^2 \times 10^{16}$, eq (A-15).....	139	57.1	182	78.8	322	107
$s \times 10^8$, eq (22).....	2.08 ± 0.26	1.48 ± 0.21	1.65 ± 0.14	1.14 ± 0.10	1.78 ± 0.12	1.06 ± 0.08
$K_s \times 10^7$, 25 °C.....	$2.85 \pm .05$	$2.59 \pm .09$	$2.84 \pm .04$	$2.52 \pm .07$	$2.85 \pm .04$	$2.56 \pm .05$
K_x , 25 °C.....		237 ± 77		297 ± 60		255 ± 35
K_y , 25 °C.....		4.8 ± 1.7		6.0 ± 1.4		5.1 ± 1.0

^a 1-Solubility product, eq (13); 2-Electroneutrality, eq (14); 3-congruent dissolution, eq (15).

^b Cases as given in the tabulation of sec. 3.5.3.

serves special consideration, particularly since such a maximum does not appear [14] in the solubility product of the closely related compound ³ CaHPO₄. It is shown below that this behavior is a possible consequence of the thermodynamic properties of the respective solids.

The van Hoff's equation provides an expression for the temperature coefficient of K_s . If the enthalpy of solution, ΔH_d^0 , for reaction (30) can be given explicitly as a function of temperature, then the temperature at which K_s has a maximum, if any, may be obtained as a root of that equation. The enthalpy of solution is given by

$$\Delta H_d^0 = \Delta H_0^0 + \int \Delta C_p dT. \quad (31)$$

The change in the heat capacity can be obtained as a function of temperature with the aid of some reasonable approximations. Furthermore, since ΔH_d^0 can be calculated at 25 °C from the corresponding value of K_s , the entropy of DCPD [21], and tabulated thermodynamic quantities [22] for the products of reaction (30), the constant ΔH_0^0 in eq (31) can be evaluated. In the present calculations using the value of K_s at 25 °C given in table 12, a value for ΔH_d^0 of -0.73 Kcal mol⁻¹ is obtained.

The heat capacity for Ca⁺⁺ (aq) was roughly estimated to be -6 cal mol⁻¹.⁴ We assumed that the heat capacity for HPO₄⁼ (aq) does not differ appreciably from the isoelectronic species SO₄⁼ [23]. The additional assumption was made that the heat capacities of water and the aqueous ions did not change with temperature over the range considered. The temperature dependence of the heat capacity, C_p , of crystalline DCPD (and that for CaHPO₄) was obtained by a least squares fitting of an equation of standard form to the data of Egan and Wakefield [21, 24],⁵ with the results (cal mol⁻¹)

$$C_p(\text{DCPD}) = 7.582 + 0.1361T - 2.217 \times 10^{-4}T^{-2}, \quad (50-310 \text{ K});$$

$$C_p(\text{DCPA}) = 10.590 + 0.05579T - 4.896 \times 10^{-4}T^{-2}, \quad (80-310 \text{ K}).$$

In eq (31) for DCPD, ΔC_p can thus be replaced by the expression

$$\Delta C_p = -47.58 - 0.136T + 2.217 \times 10^{-4}T^{-2}$$

and ΔH_0^0 is then found to be 19.58 Kcal mol⁻¹. Then the van Hoff's equation takes the form

$$R \frac{\partial}{\partial T} \ln K_s(\text{DCPD}) = -\frac{22.2}{T^3} + \frac{19.6}{T^2} - \frac{0.0476}{T} - 6.81 \times 10^{-5}.$$

The pertinent root of this equation corresponds to a maximum at 17 °C, which is in satisfactory agreement with the plot in figure 2. A variation of ± 10 percent in the assumed value for the $C_p(\text{HPO}_4^{=})$ and the use of -9 cal mol⁻¹ for $C_p(\text{Ca}^{++})$ did not affect this result significantly.

Similar calculations for DCPA indicated a maximum in K_s , far below the experimental range (i.e., ca -22 °C); although this finding is not physically meaningful, it is consistent with the observed [14] monotonic decrease in K_s for this compound in the range 5 to 37 °C.

In view of the approximations and assumptions used in the calculations, only the qualitative aspects of these results are to be emphasized. They show that the presence of a maximum in the K_s of DCPD, which contrasts with the monotonic decrease in that of DCPA, is consistent with the results of calculations based on the known thermodynamic properties of these compounds.

c. Association Constants and Bjerrum's Theory

The relationship of the association constant and the distance, a , between the constituent ions in an ion pair was derived by Bjerrum [25] on the basis of Coulombic forces

³ It may be pointed out that the salt CaSO₄ · 2H₂O, which is isostructural with DCPD, does show a maximum in its solubility near 15 °C [20], although it can not be inferred from this that a maximum exists in its solubility product.

⁴ Values of the necessary partial molar heat capacities at infinite dilution (cal mol⁻¹) are (1) for Cl⁻, -32.6 [22]; (2) for CaCl₂, -71 , kindly estimated by Dr. Vivian B. Parker of the National Bureau of Standards, Thermochemistry Section, by a rough extrapolation from the available data. A check on the value of -6 for Ca⁺⁺ derived in this way was obtained by using the value -74.4 for BaCl₂ given in table (8-4-3) of reference [26]; a value of -9 was estimated in this way.

⁵ Only "normal" points in reference [24] included.

$$K_{\text{assoc.}} = \frac{4\pi N}{1000} \left[\frac{|z_1 z_2| \epsilon^2}{DkT} \right]^3 Q(b), \quad (32)$$

with

$$b = \frac{|z_1 z_2| \epsilon^2}{aDkT}.$$

Values for the function $Q(b)$ have been calculated by various investigators and summarized by Harned and Owen [26]. The use in eq (32) of the extreme values of the 95 percent confidence interval for $K_x(25^\circ\text{C})$ and $K_y(25^\circ\text{C})$ reported here, yielded the ranges 3.8–4.5 Å and 5.9–6.1 Å for the a parameters of $[\text{CaHPO}_4^0]$ and $[\text{CaH}_2\text{PO}_4^+]$, respectively. Larger values of a are expected for $[\text{CaH}_2\text{PO}_4^+]$ than for $[\text{CaHPO}_4^0]$ on the basis of the valences of the constituent ions in the two ion pairs.

Considering the interatomic distances usually found in calcium phosphates [27] and assuming sharing of the PO_4 -tetrahedron edge by the calcium, the distance between the phosphorous and calcium atoms would be in the order of 3 Å. The apparent consistency between this result and the a values calculated above should be taken cautiously because if the two ions were indeed that close, polarization effects, not considered in equation (32), would undoubtedly play a role. It is pertinent to point out that in the investigation by Dunsmore and James [28] on the dissociation of $[\text{MgSO}_4^0]$ (isoelectronic with $[\text{CaHPO}_4^0]$), the results of their conductivity measurements could be explained on the basis of eq (32), and were consistent with a value of 5.1 Å for a .

5.3. Comparison With Reported Data

Greenwald et al. [29] studied the formation of the ion pair $[\text{CaHPO}_4^0]$ in mixtures containing H_3PO_4 , NaOH , and CaCl_2 . From their pH measurements with a glass electrode (presumably at 25°C) and also with a hydrogen electrode at 25°C they calculated instability constants at various ionic strengths; in their calculations, ionic concentrations were used instead of activities. The equation used by Greenwald et al. [29], to describe the dependence of their values on ionic strength yields a stability constant $K_x = 316$ for infinite dilution, in reasonable agreement with the value $K_x(25^\circ\text{C}) = 255$ reported here.

Davies and Hoyle [30] reported instability constants at 25°C for systems containing sodium and potassium phosphate buffers saturated with respect to CaIO_3 ; their pH measurements were made colorimetrically. The range of values obtained by Davies and Hoyle, $K_x(25^\circ\text{C}) = 417$ to 625 and $K_y(25^\circ\text{C}) = 11.5$ to 12.5 , agree in order of magnitude with those reported here.

Greenwald [31] used the measurements reported by Bjerrum [32] in the dilute range of the homogeneous system $\text{Ca}(\text{OH})_2\text{—H}_3\text{PO}_4\text{—H}_2\text{O}$ at 18°C to calculate values for the instability constant of $[\text{CaHPO}_4^0]$; these varied from 1.01 to 9.55×10^{-3} . The average value, 2.77×10^{-3} , yields a $K_x(18^\circ\text{C}) = 1/(2.77 \times 10^{-3}) = 361$, agreeing in order of magnitude with the value reported here at 15°C . Greenwald [31] also recalculated the value of K_x from the data of Davies and

Hoyle [30]; for this purpose, he calculated the pH from the experimental buffer ratios; his values for K_x thus obtained covered the range from 56 to 100. As in previous reports by the same author [29, 33], ionic concentrations instead of activities were used in these calculations. Therefore, only order of magnitude agreement with the values reported here is significant.

Similar rough agreement is found with the result of Gosselin and Coghlan [34], $K_x(25^\circ\text{C}) = 72$, who also used ionic concentrations instead of activities in their calculations.

Recently, Chughtai et al. [35] have reported stability constants for the species $[\text{CaH}_2\text{PO}_4^+]$, $[\text{CaHPO}_4^0]$, and $[\text{CaPO}_4^-]$ calculated from pH measurements in the system $\text{KOH—NaOH—H}_3\text{PO}_4\text{—CaCl}_2\text{—H}_2\text{O}$. By working in a low pH region (where the concentrations of the neutral and negatively charged species are negligible) those investigators calculated $K_y(25^\circ\text{C}) = 25.6$; this value was then used in systems at higher pH values to calculate $K_x(25^\circ\text{C}) = 548$; reported values at 37°C were $K_y(37^\circ\text{C}) = 31.9$ and $K_x(37^\circ\text{C}) = 681$.

In the calculations of Chughtai et al. [35], the equation describing the condition of electrical neutrality was solved algebraically with the measured concentrations and pH values considered exempt of error. Calculations based on perfect compliance of the data to the electroneutrality condition are extremely sensitive to small experimental errors; this was an important factor in the adoption of the statistical procedure reported in this paper. Furthermore, by the procedure of Chughtai et al. [35], the two constants are obtained as ostensibly independent quantities, whereas in fact, a strong correlation should be expected.

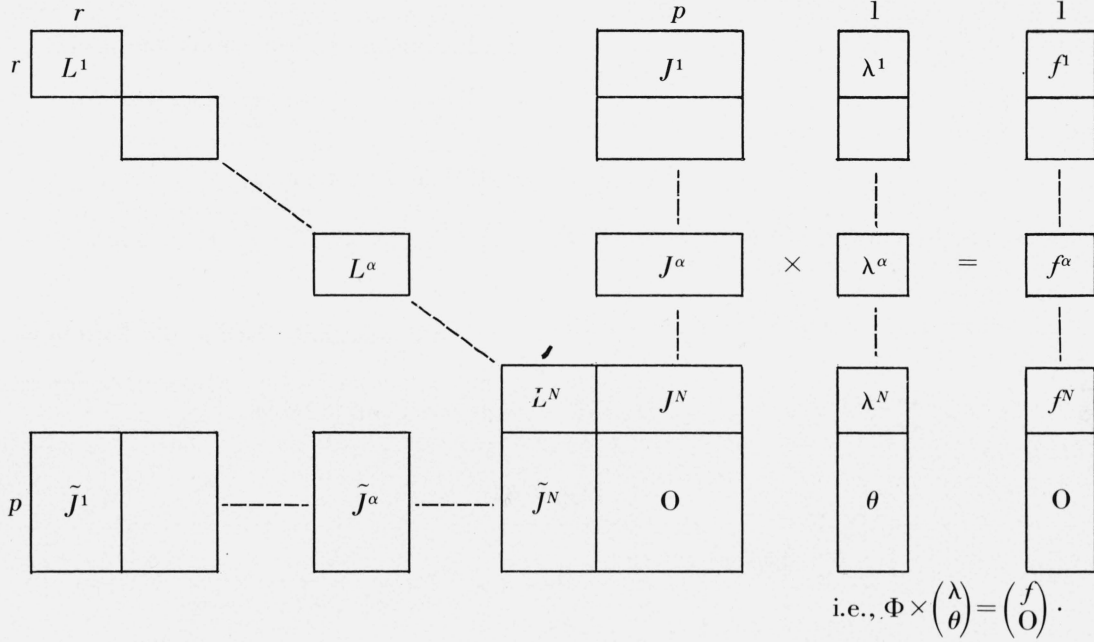
The use in eq (32) of the values for K_x and K_y at 25°C reported by Chughtai et al. yields values of 3.1 Å and 2.3 Å for the interionic distance parameters for $[\text{CaHPO}_4^0]$ and $[\text{CaH}_2\text{PO}_4^+]$, respectively. This is an unreasonable result in view of the crystallographic radii of the ions involved [27], and, furthermore, contradicts the expectation $a[\text{CaH}_2\text{PO}_4^+] > a[\text{CaHPO}_4^0]$ (sec. 5.2c).

6. Appendix

6.1. Generalized Least Squares for Independent Systems

In this paper attention is focused on individual systems and this is reflected in the notation of table 1 by the use of the superscript α to denote the α th system. Apart from this feature, our notation differs from that of reference [4] in the following respects: (1) n and r designate here the number of components in the α th observation and condition function vector, respectively, with $\alpha = 1, \dots, N$; in table [11.3.3], n and r refer to the total of such components for N systems. (2) The correction vector θ with components θ_ν replaces $-b$. (3) The vector of adjustable constants (parameters) is here denoted by β with initial values β^0 . The definitions of reference [4] are inconsistent. The

equation $b_j = b_j^0 + b_j'$, following [11.3, 1], uses b_j and b_j^0 like β_ν and β_ν^0 , with $-b_j = \vartheta_\nu$. Elsewhere b^0 is consistently used like β^0 , but b appears in table [11.3.3] and subsequent equations as the correction vector. (4) The matrices J^α and F^α are the transposes of submatrices of J and F . Transposed matrices are indicated by the tilde.



The matrix Φ is readily inverted by the method of submatrices [36] with the result

$$\Phi^{-1} = \chi = \begin{pmatrix} [\chi^{\alpha\beta}] & [\chi^{\alpha p}] \\ [\chi^{p\alpha}] & -C^{-1} \end{pmatrix}, \quad (\text{A-1})$$

where

$$\chi^{\alpha\beta} = L^{\alpha-1} \delta_{\alpha\beta} - L^{\alpha-1} J^\alpha C^{-1} \tilde{J}^\beta L^{\beta-1}, \quad (\text{A-2})$$

$$\chi^{p\alpha} = C^{-1} \tilde{J}^\alpha L^{\alpha-1}, \quad (\text{A-3})$$

and C is defined by eq (18). In eq (A-2) $\delta_{\alpha\beta}$ is the Kronecker delta. Since the submatrices of χ^{rr} and χ^{pr} are $\chi^{\alpha\beta}$ and $\chi^{p\alpha}$, respectively, solutions analogous to [11.3.3.1, 1c] may be written as linear combinations of the multivariate vectors f^α :

$$\lambda^\alpha = \sum_\beta \chi^{\alpha\beta} f^\beta, \quad (\text{A-4})$$

and

$$\theta = \sum_\beta \chi^{p\beta} f^\beta. \quad (\text{A-5})$$

The last equation, by virtue of the definition (A-3), is just the solution of the reduced normal equations, eq (17).

a. Solution of the General Normal Equations

In order to determine the specific covariance matrices needed in these calculations it is necessary to identify the submatrices of χ , [11.3.3, 2]. The system of eqs [11.3.3.1, 1a] adapted to the analysis used in this paper can be exhibited in diagrammatic form as follows:

b. Covariance Matrices

Observations. The observations Y_i^α are independent for all α and i , and therefore

$$\mathcal{E}(\delta Y_i^\alpha \delta Y_j^\beta) = s^2 w_{ii}^{-1} \delta_{ij},$$

and

$$\text{Cov}(y^\alpha, y^\beta) = \mathcal{E}(\delta y^\alpha \delta y^\beta) = s^2 W^{\alpha-1} \delta_{\alpha\beta}. \quad (\text{A-6})$$

Conditions functions. The analogue of [11.3.3.1, 5b] for a pair of vectors is

$$\text{Cov}(f^\alpha, f^\beta) = s^2 F^\alpha W^{\alpha-1} \tilde{F}^\beta \delta_{\alpha\beta} = s^2 L^\alpha \delta_{\alpha\beta}. \quad (\text{A-7})$$

Other covariance matrices. The following are submatrices of the indicated covariance matrices derived in [4]:

(1) Lagrangians [11.3.4, 2a]

$$\text{Cov}(\lambda^\alpha, \lambda^\beta) = s^2 \chi^{\alpha\beta}. \quad (\text{A-8})$$

(2) Residuals [11.3.4.1, 2a]

$$\text{Cov}(V^\alpha, V^\beta) = s^2 W^{\alpha-1} \tilde{F}^\alpha \chi^{\alpha\beta} F^\beta W^{\beta-1}. \quad (\text{A-9})$$

(3) Adjusted observations [11.3.4.2, 3b]

$$\text{Cov}(U^\alpha, U^\beta) = s^2 W^{\alpha-1} \delta_{\alpha\beta} - \text{Cov}(V^\alpha, V^\beta) = s^2 \omega^{\alpha\beta}.$$

(A-10)

c. Residuals and Sum of Squares

The individual residuals vectors are subvectors of [11.3.4.1, 1]:

$$V^\alpha = W^{\alpha-1} \tilde{F}^\alpha \lambda^\alpha \quad (\text{A-11})$$

and the weighted sum of squares is

$$q^2 = \sum_\alpha \tilde{V}^\alpha W^\alpha V^\alpha. \quad (\text{A-12})$$

This expression can be converted into a form more convenient for testing for convergence as follows: With the substitution of eq (A-11) for V^α and the subsequent identification $L^\alpha = F^\alpha W^{\alpha-1} \tilde{F}^\alpha$ by eq (A-7), (A-12) becomes

$$q^2 = \sum_\alpha \tilde{\lambda}^\alpha L^\alpha \lambda^\alpha. \quad (\text{A-13})$$

Now, with the aid of (A-2), (A-3) and (A-5), (A-4) for λ^α can be converted into

$$\lambda^\alpha = L^{\alpha-1} (f^\alpha - J^\alpha \theta). \quad (\text{A-14})$$

With the substitution of (A-14) into (A-13) we get

$$q^2 = \sum_\alpha (\tilde{f}^\alpha - \tilde{\theta} \tilde{J}^\alpha) L^{\alpha-1} (f^\alpha - J^\alpha \theta);$$

carrying out the multiplication and using

$$C\theta = \sum_\alpha \tilde{J}^\alpha L^{\alpha-1} f^\alpha,$$

eq (17), the final result is

$$q^2 = \sum_\alpha \tilde{f}^\alpha L^{\alpha-1} f^\alpha - \tilde{\theta} C\theta. \quad (\text{A-15})$$

6.2 Constants Used in the Calculations

The values for the temperature-dependent constants are given in table A1.

TABLE A1

$t^\circ\text{C}$	Phosphoric Acid			Water $10^{14}k_w[39]$	$A(T)[40]$	$B(T)[40]$
	$10^3k_1[37]$	$10^7k_2[16]$	$10^{12}k_3^a$			
5	0.845	0.523	0.226	0.1846	0.4952	0.3256
15	.782	.587	.320	0.4505	.5028	.3273
25	.711	.636	.452	1.008	.5115	.3291
37.5	.618	.659	.692	2.485	.5242	.3318

^a From the equation $pK_3 = 12.45 - (t^\circ\text{C} - 18) \times 0.015$ of [38].

The values of the inter-atomic distance parameter a_i used here are listed in table A2.

TABLE A2

	H_2PO_4^-	HPO_4^{2-}	PO_4^{3-}	H^+	OH^-	Ca^{++}
$10^8 a_i[41]$	4	4	4	9	3.5	6

7. References

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